DC And AC Conductivity Of Chitosan-Silver Triflate Polymer Electrolyte

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Abstract

The frequency and temperature dependence of to DC and AC conductivity of chitosan-silver triflate electrolyte has been studied from 303 K to 423 K and over a frequency range of 50 Hz to 1000 kHz. The conductivity was found to increase with the increase in $AgCF_3SO_3$ concentration. The DC conductivity increases in the low temperature region but decreases at higher temperatures. From the total conductivity versus frequency plots, dispersion from DC to AC conductivity can be observed below 358 K.

Keywords: chitosan, silver triflate, DC conductivity, AC conductivity

1. INTRODUCTION

Studies on solid polymer electrolytes (SPE) have been progressing actively due to their potential application in solid state electrochemical cells, high energy density batteries, fuel cells, sensors and electrochromic devices [1-2]. Polymer electrolytes have good mechanical properties, can be easily fabricated as thin films, can have a wide range of composition allowing control of properties and are able to form effective electrode-electrolyte contacts. Many types of polymer electrolytes have been studied in the pursuit to develop solid electrolyte systems [3]. These include PVA [4], PVC [5-7], PPG4000 [8], PEO [9-11] and PVdF [12].

Chitosan is a natural and low cost biopolymer. It is biocompatible, non-toxic and chemically and thermally stable. Chitosan has been widely studied as a promising source of membrane materials. According to Cui et al. [13] chitosan can be used in the preparation of polyelectrolyte complexes via electrostatic interactions with polyanions. Previous studies have proven that chitosan can be used as a polymer matrix for ionic conduction. Each of the nitrogen and oxygen atoms in chitosan has lone pair electrons where complexation can occur. Thus, chitosan satisfies one of the criteria as pointed out by Armand and Gray for the chitosan to act as a polymer host for the solvation of salts [14]. Usually both crystalline and amorphous phases are present in polymer electrolytes but conductivity mainly occurs in the amorphous phase [15]. Some ion-conducting polymer electrolytes based on chitosan have been reported. Examples include chitosan doped with ammonium nitrate (NH_4NO_3) [16], ammonium triflate ($NH_4CF_3SO_3$) [17] and silver nitrate ($AgNO_3$) [18] and ammonium iodide (NH_4I) [19].

To the best of our knowledge, there are no reports in the literature which discuss the effect of silver triflate on the chitosan polymer. Silver polymer electrolytes comprising silver salts dissolved in a polar polymer matrix other than chitosan have attracted much attention for their application in solid state membranes. These silver solid polymer electrolytes (SPE) have many advantages, including high separation performance, simple operation and low energy consumption [20]. In view of the above reasons, the present paper aims to (i)

study the influence of silver triflate ($AgCF_3SO_3$) salt at low concentration on the DC conductivity of chitosan, and (ii) to study the effect of temperature and frequency on the AC conductivity of chitosan-silver triflate.

2. EXPERIMENTAL

2.1 Preparation Of SPE Films

Chitosan from crab shells (≥ 75 % deacetylated, Sigma) and silver triflate with relative molecular weight 256.94 (supplied by Fluka, ≥ 98 purity) have been used as the raw materials in this study. The SPE films were prepared by the solution cast technique. For this purpose 1 g of chitosan was dissolved in 100 ml of acetic acid (1 %) solution. The mixture was stirred continuously with magnetic stirrer for several hours at room temperature (333 K) until the chitosan powder has completely dissolved in acetic acid solution. To this set of solutions, 2 wt. % to 10 wt. % silver triflate were added separately and the mixtures were stirred continuously until homogeneous solutions were obtained. The solutions were then cast into different clean and dry plastic petri dish and left to dry at room temperature in order to allow complete evaporation of solvent for obtaining solvent-free films of the polymer host and polymer salt complexes, respectively. The films were kept in desiccators with silica gel desiccant for further drying. Table 1 shows the concentration of the prepared samples.

Table 1 The composition of chitosan doped with silver triflate

Designation	Chitosan (g)	$AgCF_3SO_3$ (g)	Silver triflate (wt. %)
CA	1.0	0.0000	0.0
CA1	1.0	0.0204	2.0
CA2	1.0	0.0416	4.0
CA3	1.0	0.0638	6.0
CA4	1.0	0.0869	8.0
CA5	1.0	0.1111	10.0

2.2 Complex Impedance Spectroscopy

The complex impedance spectroscopy is used to characterize the electrical properties of the materials. The SPE films were cut into small discs of 2 cm diameter and sandwiched between two stainless steel electrodes under spring pressure. The complex impedance plot that is (Z'' versus Z' where Z' and Z'' represent the real and imaginary parts of impedance respectively) were used for the evaluation of the electrical conductivities of various samples as a function of temperature. The electrical conductivity was calculated using the relation,

$$\sigma = \frac{t}{R_b A} \qquad (1)$$

where, t is the thickness, A is the area of the film and R_b is the bulk resistance of the film derived from the intercept of the impedance plot on the real axis.

3. RESULTS AND DISCUSSION

3.1 DC conductivity

The room temperature conductivity of chitosan-$AgCF_3SO_3$ is shown in Fig. 1.

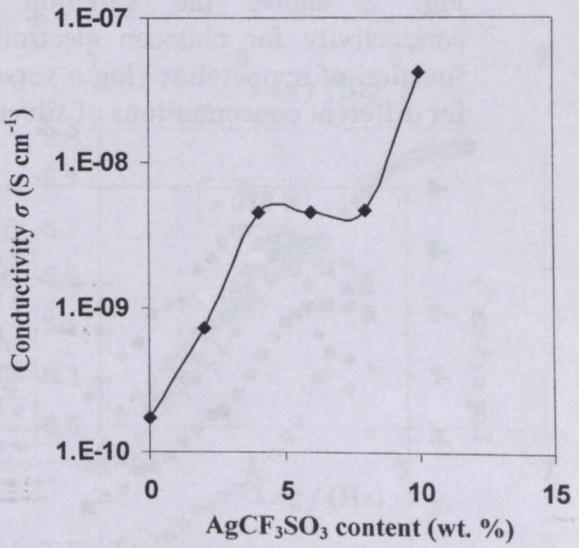

Fig. 1 The ionic conductivity of chitosan with various concentrations of $AgCF_3SO_3$

Note that the ionic conductivity of chitosan electrolyte increases with increasing $AgCF_3SO_3$ concentrations. The conductivity value in room temperature has been found to increase by an order of magnitude from 1.73

$\times 10^{-9}$ for pure chitosan polymer to 4.25 $\times$ 10^{-8} S cm^{-1} at 0.1 % $AgCF_3SO_3$ doping level. This indicates the fact that dissociation of silver triflate has taken place within the polymer electrolyte.

The general expression for conductivity is

$$\sigma = n q \mu \qquad (2)$$

where n is the concentration of charge carriers, q is 1.6 $\times$ 10^{-19} C, and μ is the mobility of the ions. Thus, a steep increase in conductivity can be explained by an increase either in mobility or in the concentration of charge carriers [21]. Relatively few studies have been reported on polymers complexed with silver salts. The reported conductivities are all within the range from 10^{-8} to 10^{-5} S cm^{-1}, except for PEO-$AgNO_3$ where conductivity as high as 9 $\times$ 10^{-3} S cm^{-1} has been found for extremely high concentrations of the silver salt [22]. The conductivity values reported for $AgNO_3$+PEO, $AgNO_3$+poly(pentamethylene sulfide) and AgI+NaI+PEO [21] are very close to the present paper for chitosan+$AgCF_3SO_3$.

Fig. 2 shows the variation of DC conductivity for chitosan electrolyte as a function of temperature (log σ versus $10^3/T$) for different concentrations of silver triflate.

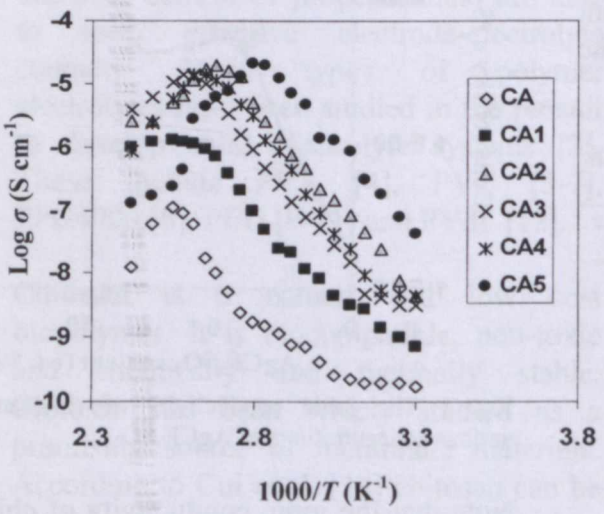

Fig. 2 Temperature dependence of ionic conductivity of chitosan-silver triflate

From Fig. 2, conductivity increases with increasing temperature up to a certain temperature, which changes with salt concentration, after which the conductivity begins to decrease. In the region where conductivity increases with temperature, there is no sudden change in the value of conductivity with temperature. According to Yahya et al. [21], the non-existence of any abrupt jump indicates the fact that the chitosan-based electrolyte is completely amorphous.

The linear increase in conductivity of the chitosan electrolyte with increase in temperature can be described by the Arrhenius equation,

$$\sigma = \sigma_0 \exp(-E_a / k_B T) \qquad (3)$$

Here σ is the conductivity at temperature, T (in Kelvin), k_B is the Boltzmann constant, E_a is the activation energy and σ_o is the pre-exponential factor. The activation energy, E_a may be deduced easily from the slope of log σ versus $1000/T$ plot. The activation energy indicates the energy barrier an ion has to overcome for a successful jump between sites [24]. The calculated activation energy, E_a decreases from 0.99 eV to 0.81 eV as the conductivity of the sample increases. The increase in conductivity may be attributed to the increase in dielectric constant of the sample. Dielectric constant is known to increase with temperature. The decrease in conductivity with increasing temperature may be ascribed to the scattering of carriers due to the increased vibrations of functional groups at these elevated temperatures [25].

3.2 AC Conductivity Versus Frequency

The total conductivity, $\sigma_{(\omega)}$ of chitosan based electrolyte for the highest conducting sample has been studied as a function of frequency from 50 Hz to 1000 kHz and 303 K to 423 K. The total conductivity on can be expressed by the following equation [25]

$$\sigma_{(\omega)} = \sigma_{dc} + A\omega^s \quad 0 < s < 1 \qquad (4)$$

Here σ_{dc} is the conductivity that is independent of frequency. The frequency variation of total conductivity ($\sigma_{(w)}$), at different temperatures is shown in Fig. 3.

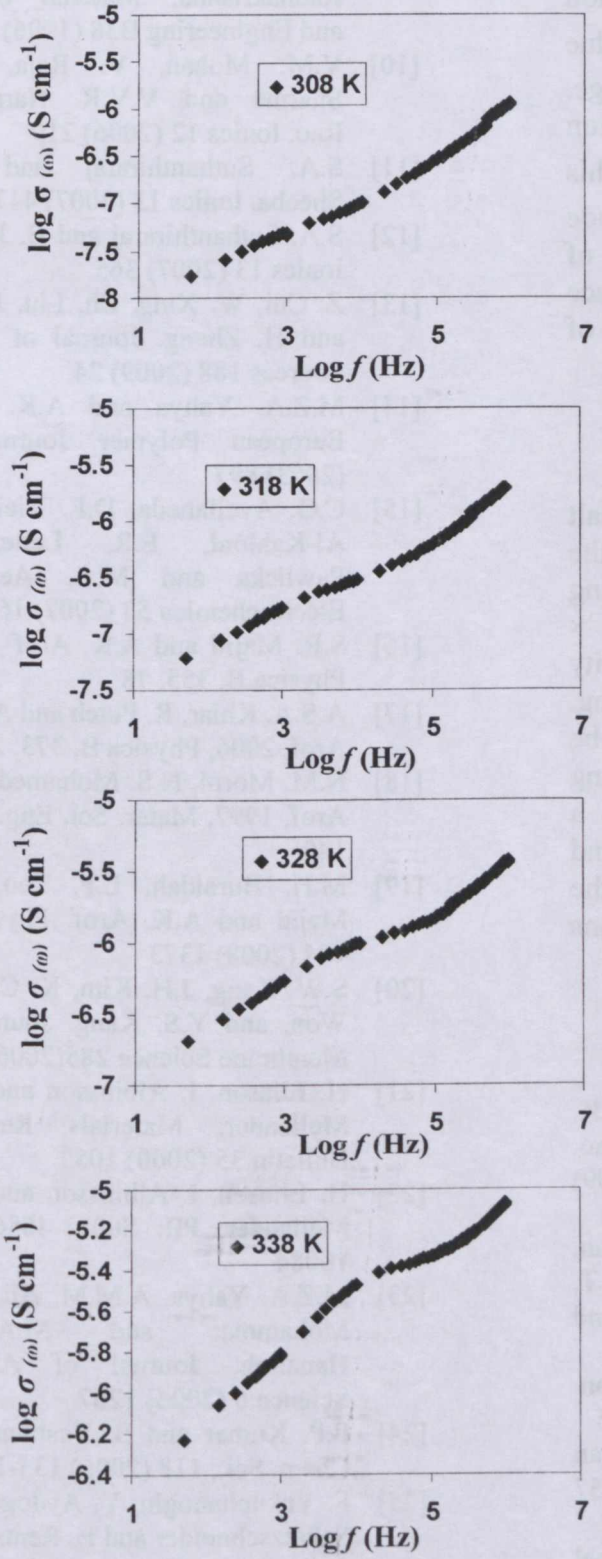

Fig. 3 Frequency dependence of $\sigma_{(\omega)}$ at various temperatures for CA5

$\sigma_{(\omega)}$ increases with increasing in frequency up to 338 K. Above this temperature $\sigma_{(\omega)}$ seems to saturate at high frequencies. This frequency dependence of conductivity

suggests the hopping conductivity and follows the Jonschers power law behavior [26]. At 308 K dispersion between electrode polarization, σ_{dc} and σ_{ac} is not that obvious. At 318 K to 348 K, the dispersion is clearer. However at 358 K, dispersion between σ_{dc} and σ_{ac} is not observed due to limitation of the frequency range. Dispersion between electrode polarization and σ_{ac} is however clearly manifested. This continues at even of 378 K. Electrode polarization indicates the accumulation of ions at the electrode-electrolyte interface and that the ions have a distribution of relaxation times.

4. CONCLUSIONS

In conclusion, in the range of salt concentration between 0 to 10 wt. %, the conductivity for the highest conducting sample in chitosan - $AgCF_3SO_3$ is 4.25×10^{-3} S cm^{-1}. The results for DC conductivity indicate that the ions conduct by hopping. The DC activation energy was found to be about 0.81 eV for the highest conducting sample. The conductivity demonstrated a frequency and temperature dependence and obeys the power law. Conductivity in the low frequency region indicates that the ions have a distribution of relaxation times.

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